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# Reactions of VX, GD, and HD with Nanosize CaO: Autocatalytic Dehydrohalogenation of HD

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# Reactions of VX, GD, and HD with Nanosize CaO: Autocatalytic Dehydrohalogenation of HD

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Room-temperature reactions of the chemical warfare agents VX, GD, and HD with nanosize CaO (AP-CaO), and HD with commercial CaO have been studied using solid-state MAS NMR. VX and GD hydrolyze to yield surface-bound complexes of nontoxic ethyl methylphosphonate and pinacolyl methylphosphonate, respectively. The kinetics are characterized by an initial fast reaction followed by a slower, diffusion-limited reaction. Similar behavior is observed for HD on either dried or hydrated AP-CaO and CaO. On partially hydrated AP-CaO (but not CaO), a rather fast steady-state elimination of HCl occurs after an induction period. This behavior is attributed to acid-catalyzed surface reconstruction (to regenerate fresh surface) and the formation of $CaCl_2$, which is known to be more reactive than CaO. The product distribution for HD is about 80% divinyl sulfide and 20% thiodiglycol and/or sulfonium ions, which apparently reside as surface alkoxides. Such kinetic behavior was not evident for the common mustard simulant 2-chloroethyl ethyl sulfide (CEES) on partially hydrated AP-CaO, which exhibited only the typical fast/diffusion-limited reaction.

## Introduction

Inorganic oxide particles are currently under consideration as reactive adsorbents for the decontamination of chemical warfare agents.[1] Enhancement in the reactivity of nanosize oxides is anticipated owing to increased surface area, greater amounts of highly reactive edge and corner "defect" sites, and unusual, stabilized lattice planes.[2] We recently reported results for the room-temperature reactions of neat liquid VX, GD, and HD with nanosize MgO (AP-MgO), which showed facile room-



VX　　　　　GD　　　　　HD
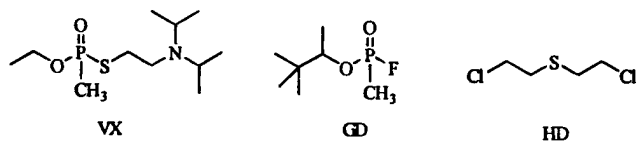
temperature reactivity for all three agents, although liquid-state diffusion limitations severely reduced the overall reaction rates.[3] VX and GD (Soman) are "nerve" agents, and HD (mustard) is a "blister" agent.[1a]

Metal oxides such as MgO and CaO are known to effect the elimination of HCl from chlorinated alkanes.[4] Curiously, $CaCl_2$ (but apparently not $MgCl_2$) is reportedly even more active for this reaction than either of these oxides.[4c] The reaction of CaO with acid-forming gases such as $SO_2$ is well-known, and water vapor has a favorable effect on its complete conversion to $CaSO_3/CaSO_4$.[5] Thus the reaction is not limited to the surface, but continues through the bulk of the particle. The mechanism is not hard to envision as CaO is soluble in aqueous acid. Therefore, the formation of $CaCl_2$ from HCl generated during

the dehydrohalogenation of chlorinated alkanes is anticipated, and water should affect the extent of this conversion. In situ generation of $CaCl_2$ and the conversion of bulk CaO to $CaCl_2$ are both potentially important processes to achieve a fast, catalytic elimination of HCl from HD.

Elimination of HCl from HD was observed on AP-MgO, although a large amount of hydrolysis (ca. 50%) also occurred (Scheme 1).[3] GD and VX were observed to simply hydrolyze on AP-MgO (Schemes 2 and 3). These hydrolysis reactions are quite similar to those observed in solution,[1a] except that the resulting products form surface-bound metal phosphonates (VX and GD) and metal alkoxides[6] (HD). The vinyl and divinyl HD products are not bound to the surface and thus remain volatile. Another exception is that basic hydrolysis of VX in solution yields significant amounts of toxic EA-2192 in addition to the major nontoxic ethyl methylphosphonic acid (EMPA) product.[7] EA-2912 does not form on AP-MgO or on other inorganic oxides examined,[8] including zeolites.[9] Such product selectivity for EMPA is exhibited in solution for the slow reaction of VX with an equimolar amount of water.[10]

In the present study, solid-state MAS NMR is used to examine the reactions VX, GD, and HD with nanosize CaO (AP-CaO). An unusual and fast reaction was observed for HD on partially hydrated AP-CaO which did not appear to be diffusion-limited, implying a catalytic reaction with the surface. Therefore, reactions of HD with commercial CaO and the common HD-simulant 2-chloroethyl ethyl sulfide (CEES) with AP-CaO were also examined to determine if this behavior is peculiar to the HD/AP-CaO system.
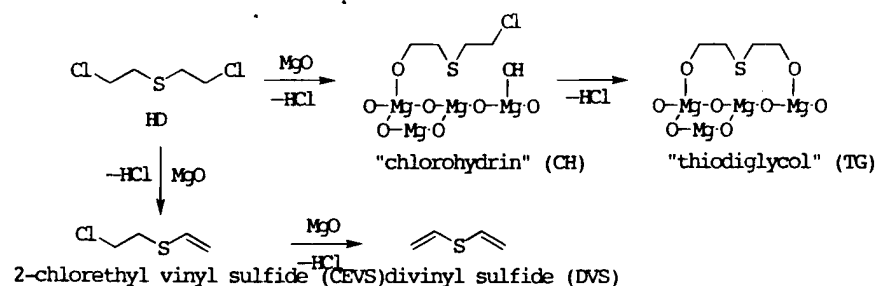
## Experimental Section

**Materials.** Nanosize CaO (aerogel-prepared, AP-CaO) was prepared as previously described.[2a] Samples prepared using the "as received" material were manipulated in air. Thus brief exposure to humid air occurred resulting in an unknown degree

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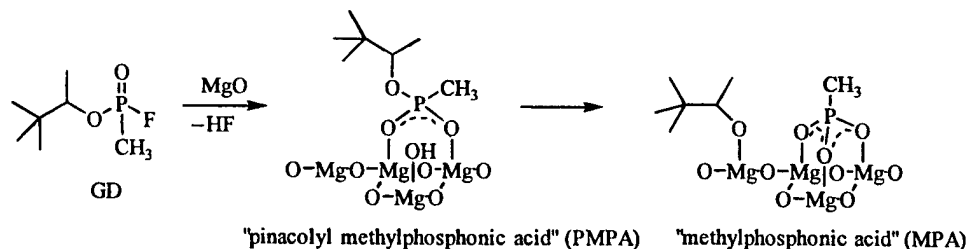\* Corresponding author. E-mail: gwwagner@sbccom.apgea.army.mil.
† Research and Technology Directorate, U.S. Army Edgewood Chemical Biological Center.
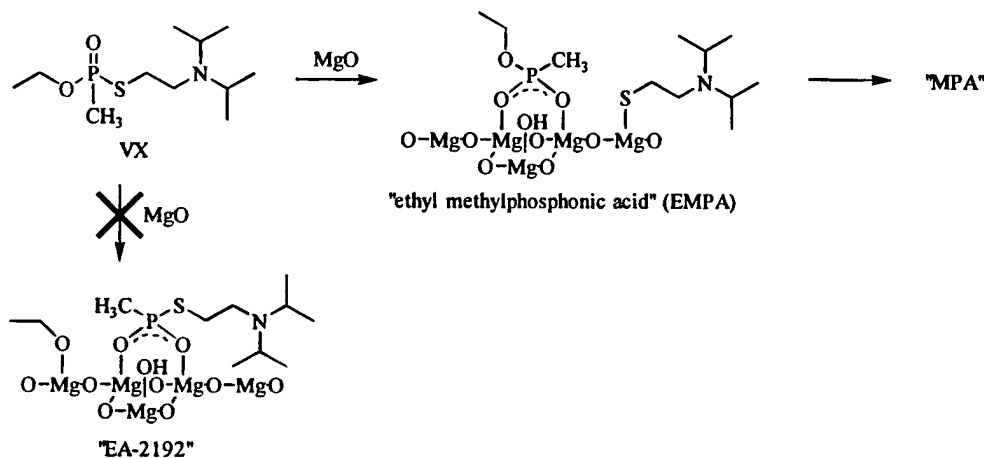‡ Department of Chemistry, Kansas State University and Nantek, Inc.

Autocatalytic Dehydrohalogenation of HD

*J. Phys. Chem. B, Vol. 104, No. 21, 2000* **5119**

**SCHEME 1**



"chlorohydrin" (CH)    "thiodiglycol" (TG)

2-chlorethyl vinyl sulfide (CEVS)    divinyl sulfide (DVS)

**SCHEME 2**



"pinacolyl methylphosphonic acid" (PMPA)    "methylphosphonic acid" (MPA)

**SCHEME 3**



"ethyl methylphosphonic acid" (EMPA)

"EA-2192"

of partial hydration. Additional hydration may have occurred during prolonged storage. Dried AP-CaO was obtained by drying in air in an oven at 100 °C overnight, resulting in a 6.2% weight loss. Wet AP-CaO was prepared by standing in air overnight at room temperature, resulting in a 9.2% weight gain. Commercial CaO (99.9%, Aldrich) was used "as received". The CaO was allowed to stand in air overnight at room temperature to obtain the "wet" material, resulting in a 5.6% weight gain. Normal and $^{13}C$-labeled HD (HD*) were used for $^{1}H$ and $^{13}C$ MAS NMR experiments, respectively. The HD* contained about 8% $CH_3C(O)OCH_2CH_2SCH_2CH_2Cl$ as an impurity.[11] Normal 2-chloroethyl ethyl sulfide (Fairfield Chemical Company) was used as received in $^{1}H$ MAS NMR experiments.

**NMR.** $^{31}P$ and $^{13}C$ MAS NMR spectra were obtained using a Varian Unityplus 300 NMR spectrometer equipped with a Doty Scientific 7 mm high-speed VT-MAS probe as previously described.[3] $^{1}H$ MAS NMR spectra were obtained using the same equipment. The nature of the HD and CEES adsorptions and reactions, i.e., no significant physisorption prior to destructive chemisorption (reaction), allowed monitoring by either $^{13}C$ or $^{1}H$ MAS NMR since the molecules remained highly mobile until their demise. In the case of $^{1}H$ MAS NMR spectra, relatively sharp peaks were evident for the mobile, volatile vinyl and divinyl products; however, peaks for the surface-bound hy-

drolysis products were too broad to detect. The latter products yielded broadened (compared to the vinyls), but detectable peaks in $^{13}C$ MAS NMR spectra.

**Reaction Procedure.** *Caution:* These experiments should only be performed by trained personnel using applicable safety procedures. In a typical run, 5 wt % neat, liquid agent or simulant (5−9 $\mu$L) was added via syringe to the center of a column of AP-CaO (ca. 120 mg) or CaO (ca. 200 mg) contained in the NMR rotor. The rotor was then sealed with the double O-ring cap. MAS NMR spectra were obtained periodically to monitor the reaction in situ.

**Results**

**GD.** Selected $^{31}P$ MAS NMR spectra obtained for 6 $\mu$L of GD added to 0.1157 g of "as received" AP-CaO are shown on the left side of Figure 1. Two doublets ($J_{PF} = 1049$ Hz) are apparent for the GD isomers centered at ca. 28.3 ppm. Over time, hydrolysis cleaves the P−F bond (Scheme 2) and the sharp doublets are replaced by a broad singlet for PMPA at 24.3 ppm. The broadness of the PMPA peak and the presence of intense spinning sidebands are indicative of surface binding of this product (Scheme 2). No further hydrolysis of PMPA to MPA was observed during the 24 h observation period. The reaction
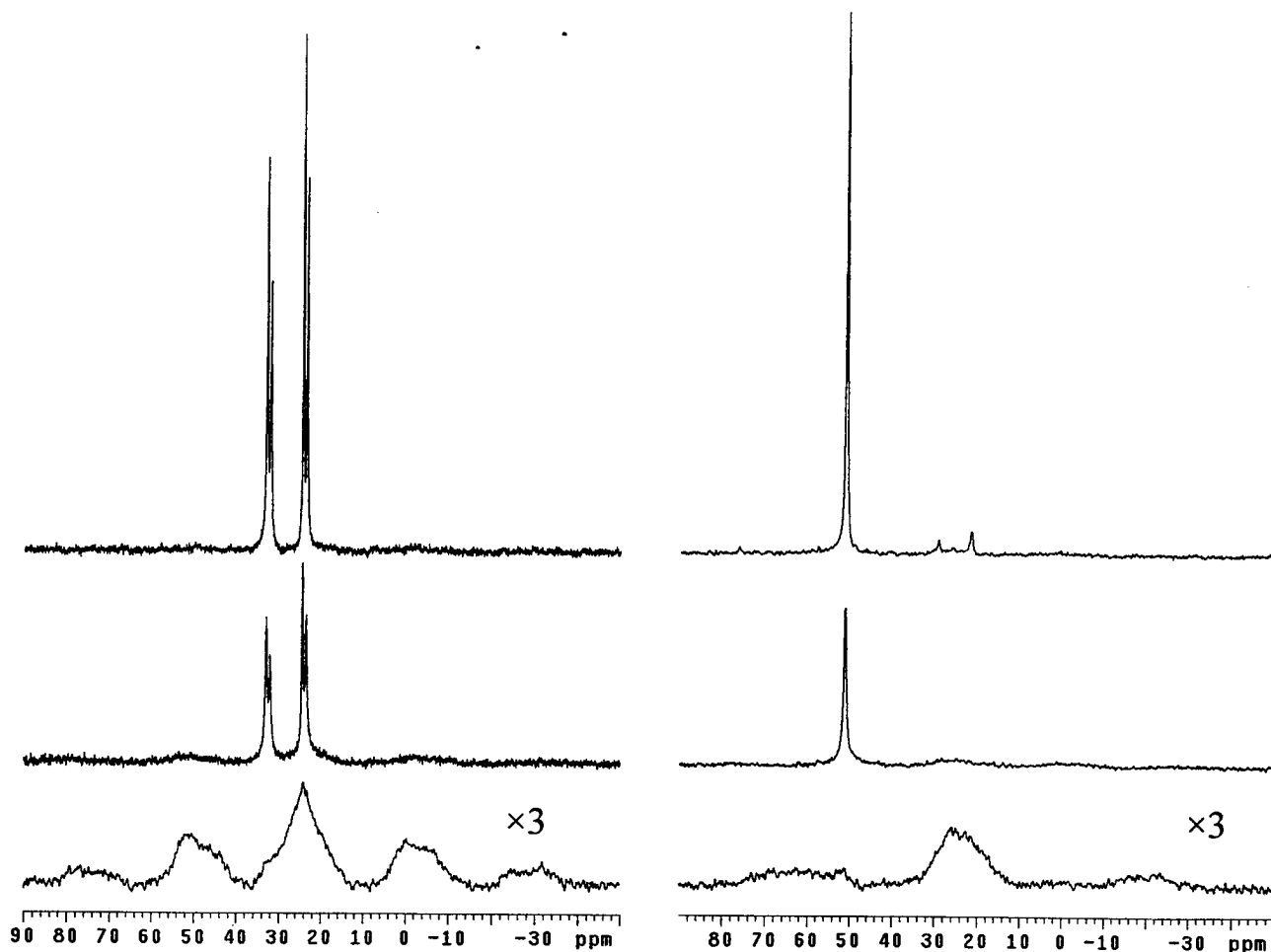
**Figure 1.** $^{31}P$ MAS NMR spectra obtained for nerve agents added to fresh, "as received" AP-CaO: (left) GD at (top to bottom) $t = 8.5$ min, 1.9 h, and 25 h; (right) VX at 8.5 min, 48 h, and 21 days. The bottom spectra for GD and VX have been expanded 3× in vertical scale.
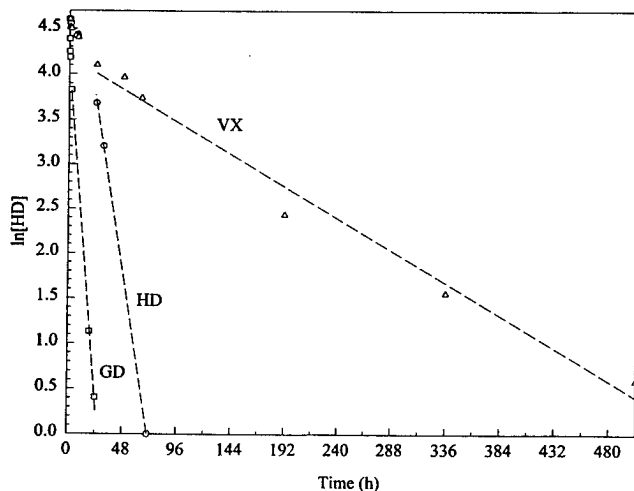


**Figure 2.** Reaction profiles for GD, VX, and HD* liquid on fresh, "as received" AP-CaO.

profile is shown in Figure 2. After a fast, initial reaction, a steady-state half-life of 4.5 h was observed.

**VX.** Selected $^{31}P$ MAS NMR spectra obtained for 6 $\mu L$ of VX added to 0.1106 g of "as received" AP-CaO are shown on the right side of Figure 1. VX yields a sharp peak at 51.1 ppm. A small amount of an impurity, VX-pyro [EtOP(O)(CH₃)OP-(O)(CH₃)(OEt)], is evident as a small peak at 21.5 ppm. Gradually, VX (and VX-pyro) hydrolyzes to EMPA (Scheme 3), which emerges as a broad peak at 25.0 ppm. Spinning

sidebands are also apparent for this surface-bound species. No peak is evident for toxic EA-2192, which would occur near 40 ppm. The reaction profile in Figure 2 shows the same behavior exhibited by GD, except that the steady-state reaction is much slower, with a half-life of 93 h.

**HD.** Selected $^{13}C$ MAS NMR spectra obtained for 5 $\mu L$ of HD* added to 0.1152 g of fresh, "as received" AP-CaO are shown on the left side of Figure 3. Peaks for HD* are present at 44.5 and 35.3 ppm. A small peak at 64.5 ppm is due to an impurity. Over time sharp peaks appear for the elimination products (see Scheme 1) at 130.6 and 114.2 ppm (DVS) and 132.0, 112.3, 43.3, and 34.4 ppm (CEVS), and broad peaks emerge for the hydrolysis product at ca. 61 and 33 ppm (TG). The broadness of the TG product peaks is indicative of surface binding as shown in Scheme 1. The products indicate the reaction proceeds via 80% elimination and 20% hydrolysis. Minor amounts of sulfonium ions derived from the hydrolysis products (see below) were also detected, and these are included in the calculation of the elimination/hydrolysis distribution. The reaction profile is given in Figure 2, which exhibits an induction period of 5 h followed by a rather fast steady-state reaction with a half-life of 8.7 h. These results are summarized in Table 1.

On the right side of Figure 3 are shown selected $^1H$ MAS NMR spectra for 9 $\mu L$ of HD added to 0.1953 g of "as received" commercial CaO. The HD peaks appear at 3.83 and 3.08 ppm. Over time the CEVS and DVS products yield overlapping vinyl proton peaks at 6.58 and 5.44 ppm; a third peak for CEVS at ca. 3.2 ppm appears as a shoulder on the HD peak. $^1H$ peaks for surface-bound TG and/or sulfonium ion products are too
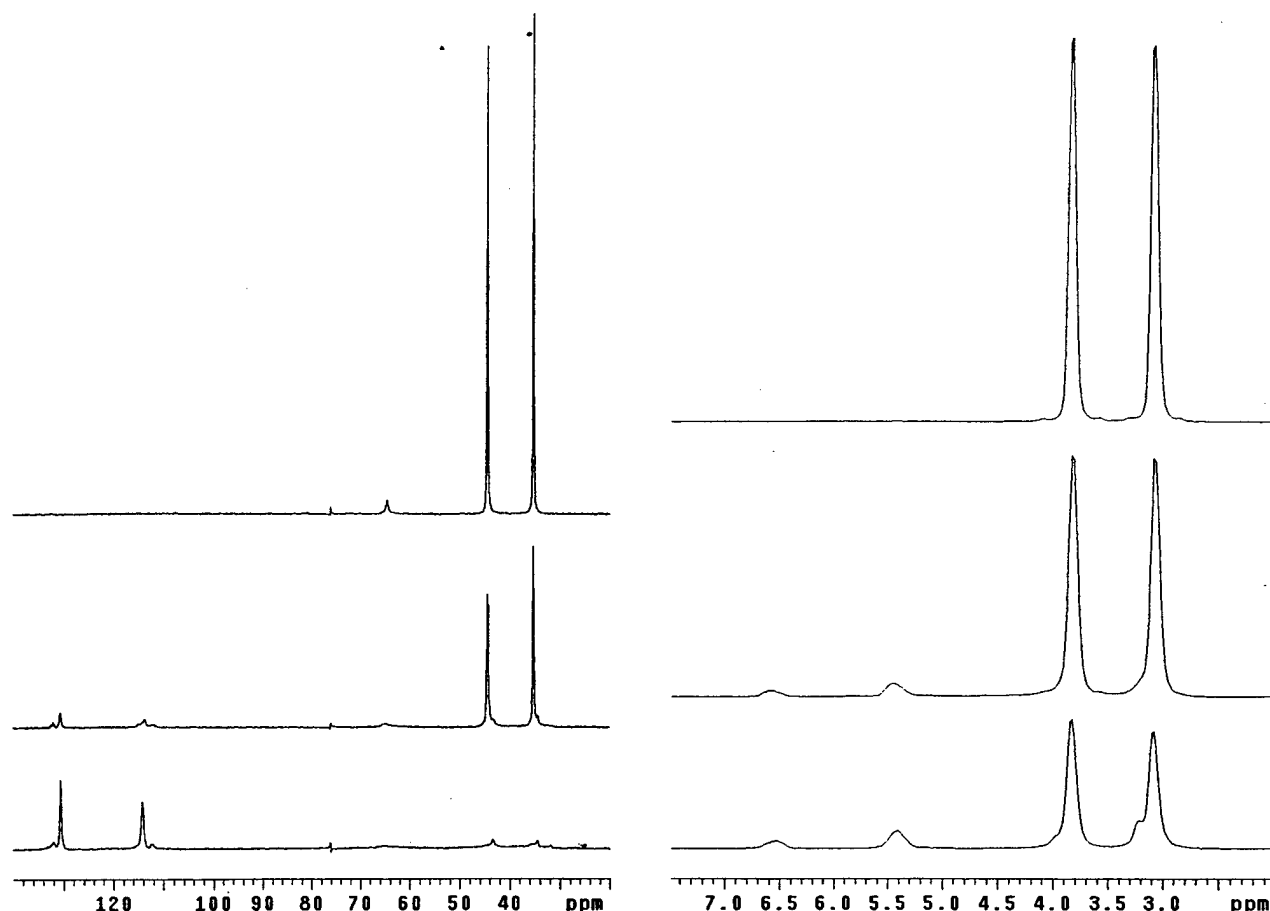
Autocatalytic Dehydrohalogenation of HD

*J. Phys. Chem. B, Vol. 104, No. 21, 2000* **5121**



**Figure 3.** MAS NMR spectra obtained for (left, $^{13}$C) HD* added to fresh, "as received" AP-CaO at (top to bottom) $t$ = 7.5 min, 6.8 h, and 70 h, and (right, $^1$H) HD added to fresh, "as received" CaO at $t$ = 8 min, 24 h, and 17 days.

**TABLE 1: HD and CEES Reactions on AP-CaO and CaO**

| compound/material/hydration | NMR method | induction period | initial half-life | steady-state half-life | elimination/hydrolysis |
|---|---|---|---|---|---|
| HD/AP-CaO/"as received" | $^{13}$C | 5 h | 8.7 h | 8.7 h | 80/20 |
| HD/AP-CaO/ aged "as received" | $^{13}$C | 1 h | 3.5 h | 3.5 h | 80/20 |
| HD/AP-CaO/ "wet" | $^{13}$C | none | 3.1 h | >46 h | 80/20 |
| HD/AP-CaO/ "dried" | $^1$H | none | 4.0 h | >11 days | 5/95 |
| HD/CaO/"as received" | $^1$H | 40 min | 31 h | >49 days | 80/20 |
| HD/CaO/"wet" | $^{13}$C | none | 9.1 h | >49 days | 60/40 |
| CEES/AP-CaO/aged "as received" | $^1$H | none | <12 min | >135 h | 5/95 |
| CEES/AP-CaO/"dried" | $^1$H | none | 1.7 h | >156 h | 30/70 |

broad to observe. The amount of vinyl product indicates about 20% elimination and 80% hydrolysis occurs. The reaction profile shown in Figure 4 exhibits a shorter induction period of about 40 min followed by a diffusion-limited reaction that continues to slow over time (final half-life > 49 days, Table 1).

Similar $^1$H or $^{13}$C MAS NMR spectra were obtained for 5 wt % HD or HD* on aged, "as received" AP-CaO ($^{13}$C), "dried" AP-CaO ($^1$H), "wet" AP-CaO ($^{13}$C), and "wet" CaO ($^{13}$C) (spectra not shown). These reaction profiles are also shown in Figure 4 and the results are summarized in Table 1. Compared to fresh, "as received" AP-CaO, the elimination of HCl from HD proceeded even faster on aged, "as received" AP-CaO, as the induction period was reduced to 1 h and the steady-state reaction exhibited a half-life of only 3.5 h. As before, about 80% elimination and 20% hydrolysis occurred. For "wet" AP-CaO, there is no discernible induction period, but the initially fast appearance of the reaction profile (intial half-life 3.1 h) is deceiving as the reaction continues to slow after 24 h (half-life > 46 h). The elimination/hydrolysis ratio for "wet" AP-CaO is still about 80/20. The "dried" AP-CaO also showed no induction period, had a somewhat slower initial half-life of 4.0 h, an even
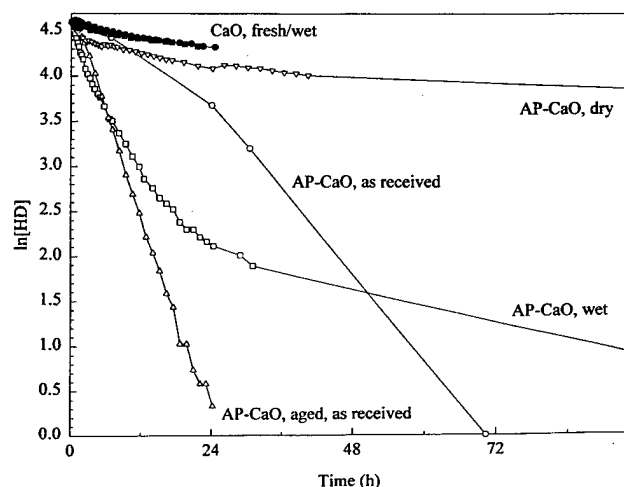


**Figure 4.** Reaction profiles for HD* and HD on AP-CaO and CaO.

slower diffusion-limited reaction (half-life > 11 days), and yielded a small elimination/hydrolysis ratio of 5/95. However,
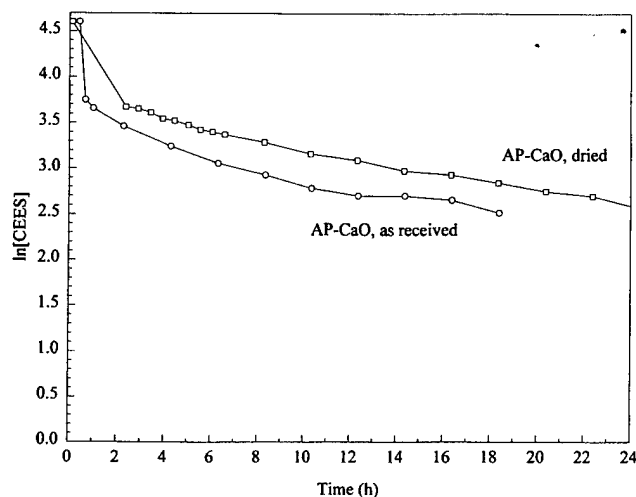
**5122** *J. Phys. Chem. B, Vol. 104, No. 21, 2000*

Wagner et al.



**Figure 5.** Reaction profiles for CEES on AP-CaO.

**SCHEME 4**



this material was still more reactive than the "as received" or "wet" CaO. "As received" CaO exhibited a short 40 min induction period and an initial half-life of 31 h, and "wet" CaO showed no induction period and a faster initial half-life of 9.1 h. However, both materials exhibited nearly identical, long-term diffusion-limited reaction profiles with extremely long half-lives greater than 49 days (Figure 4). The elimination/hydrolysis ratios were 80/20 for "as received" CaO and 60/40 for "wet" CaO.

**CEES.** Reactions of 6 $\mu$L of CEES added to ca. 0.123 g of aged, "as received" AP-CaO and "dried" AP-CaO were examined by $^1$H MAS NMR (spectra not shown). The reaction profiles are shown in Figure 5. Unlike HD, no induction period is observed for CEES on either material. As shown in Table 1, the initial CEES reactions are faster than HD, but they eventually become diffusion-limited. CEES on aged, "as received" AP-CaO and "dried" AP-CaO yielded elimination/hydrolysis ratios of 5/95 and 30/70, respectively.

**Discussion**

**GD and VX.** Hydrolysis reactions observed for GD and VX are consistent with those previously observed on AP-MgO,[3] and are adequately represented by Schemes 2 and 3. The reaction profiles are also quite similar to those observed on AP-MgO.[3] The initial, fast reaction is attributed to liquid spreading and the reaction proceeds apace. However, once the liquid achieves its volume in the pore structure, spreading stops to form a "wet spot". Since the reaction with the surface is stoichiometric (Schemes 2 and 3), the reaction halts as well. At this point, evaporation appears to be the main mechanism by which molecules in the ensconced liquid may reach fresh surface and react, leading to the slow, diffusion-limited, steady-state reactions observed. Such reactions are mediated by the evaporation rate or vapor pressure.[3] GD has a much higher vapor pressure than VX (0.4 vs 0.0007 mmHg), and thus has a much faster steady-state reaction (half-life 4.5 h) compared to VX (93 h). The half-lives observed for GD and VX are slower than those observed on AP-MgO, 28 min and 68 h,[3] respectively.

**HD.** The major reaction for HD on "as received" or "wet" AP-CaO is elimination of HCl. The elimination/hydrolysis ratio is 80/20 compared to 50/50 on AP-MgO.[3] The competing mechanisms are adequately represented by Scheme 1 with one exception, the formation of sulfonium ions. These were not detected on "as received" AP-MgO, but minor amounts were evident on AP-CaO. Sulfonium ions such as CH–TG result from the reaction of CH and TG hydrolysis products (see
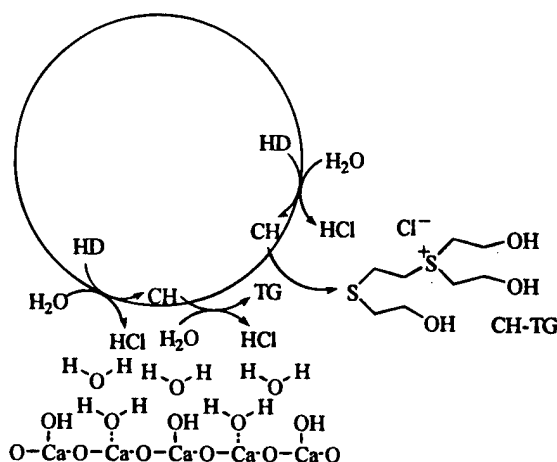
Scheme 1), and tend to form when mustard droplets are in contact with water.[12] Scheme 4 depicts this reaction for a heavily hydrated CaO surface. Hydrolyzing environments which hinder sulfonium ion formation include dilute, homogeneous solutions[12] and surfaces where destructive adsorption occurs (i.e., Scheme 1, where hydrolysis occurs at the surface and products are immediately bound, rendering them unable to react with neighboring hydrolysis products). In solution and on surfaces HD droplet formation hinders the overall hydrolysis rate since only molecules at the droplet surface react.[13] HD droplet formation is presumably also hindering the elimination reactions on the wetter materials.

HD on AP-MgO[3] showed the same kinetic behavior exhibited by GD and VX above, i.e., a fast reaction due to liquid spreading, followed by a slower, steady-state reaction mediated by evaporation. The same behavior is observed for HD on "wet" or "dried" AP-CaO and "wet" CaO. However, on partially hydrated, "as received" AP-CaO, the behavior is quite different. On this material, the kinetic behavior is characterized by an induction period which precedes a rather fast steady-state reaction which does not become diffusion-limited. Also, the major mechanism is elimination. HD on "as received" CaO exhibits features of both kinetic behaviors; i.e., a short induction period precedes a brief, fast reaction which rapidly decays to a very slow diffusion-limited reaction. The induction period and fast steady-state reaction can be attributed to the formation of CaCl$_2$ on the AP-CaO surface. CaCl$_2$ is a more active elimination catalyst than CaO.[4c] Water apparently assists in this endeavor, presumably by acid-catalyzed surface reconstruction. In this manner, the surface may be continually refreshed and expanded, resulting in the autocatalytic behavior observed. The nanosize nature of AP-CaO, i.e., small particle size and/or large amounts of unusual lattice planes and surface defect sites,[2] appears critical to achieving a sustained, catalytic elimination of HD. Moreover, AP-CaO must also possess the right amount of water. Although "as received" CaO showed evidence of a brief induction period and considerable elimination, a sustained catalytic reaction was not achieved, and this could be simply due to the larger particle size of the CaO.

**CEES.** CEES did not exhibit an induction period nor a fast, sustained catalytic elimination reaction on aged "as received" AP-CaO. On this material and on "dried" AP-CaO, the major reaction mechanism was hydrolysis, and the kinetic behavior is characterized by the typical fast/slow diffusion-limited reaction. However, the initial reactions were significantly faster than those observed for HD. The rapidity of the initial, fast CEES reaction is attributable to both its lower viscosity and

Autocatalytic Dehydrohalogenation of HD

*J. Phys. Chem. B, Vol. 104, No. 21, 2000* **5123**

surface tension, providing for faster liquid spreading,[3] and faster rate of hydrolysis relative to HD ($k = 0.0158$ s$^{-1}$ for CEES;[14] 0.00129 s$^{-1}$ for HD[15]). Consistent with this picture, no elimination products were detected for CEES during the fast reaction, and only minor elimination occurred during the diffusion-limited reaction. It may be that the rapidity of the CEES hydrolysis and the concomitant substitution of the surface with alkoxide effectively hinders the formation of the CaCl$_2$ "islands" necessary for a sustained, catalytic reaction. Consistent with this rationale, "dried" AP-CaO showed enhanced elimination activity, presumably owing to reduced water content and hydrolytic activity.

## Conclusions

AP-CaO exhibits room-temperature reactivity for VX, GD, and HD. For HD on partially hydrated AP-CaO, the presence of an induction period, the absence of a diffusion-limited reaction, and a predominant dehydrohalogenation reaction strongly suggests an autocatalytic surface reaction. Water plays a crucial role in this reaction as dried or heavily hydrated AP-CaO does not effect this behavior. The role of water may be to support an acid-catalyzed surface reconstruction to yield CaCl$_2$, which is known to be a more active dehydrohalogenation catalyst than CaO. Too much water may prevent the necessary contact or spreading of HD on the surface of AP-CaO. Although an induction period can be observed for HD on partially hydrated commercial CaO, the material does not effect the sustained, catalytic reaction behavior seen for AP-CaO, possibly due to its larger particle size and/or lack of surface morphology unique to nanosize particles. Sustained, catalytic reaction behavior is also not observed for CEES on partially hydrated AP-CaO. As hydrolysis predominates over dehydrohalogenation for CEES on AP-CaO, its relatively fast hydrolysis rate (compared to HD) and concomitant surface-alkoxide formation could hinder the formation of CaCl$_2$ "islands" necessary for facile elimination of HCl.

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